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(54) IMPROVEMENTS IN AND RELATING TO A COMPOSITE MATERIAL CONSISTING OF GLASS AND PLASTICS FILM

(71) We, KALLE AKTIENGESELLSCHAFT, a body corporate organised according to the laws of Germany, of 190-196 Rheingaustrasse, Wiesbaden-Biebrich, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention is concerned with improvements in and relating to a composite material consisting of glass and plastics film.

The production of composite structures of glass and plastics film has been known for a long time. Thus, glass fibres have been added to melts for the production of plastics films in order to impart to the plastics films specific mechanical properties, such as improved slip qualities. Other composite materials consisting of glass and plastics material include shaped plastics articles reinforced by glass fibres, or the well-known safety glasses, in which a layer of a plastics material is sandwiched between glass plates to prevent serious fragmentation when the material is damaged.

Recently, it has become possible to produce glass foils in the form of webs or plates of a thickness of not more than about 5 μm, which foils are distinguished by high flexibility, but have the disadvantage of being brittle and of low impact strength. In the plastics industry, films are produced which have a thickness in the range from 1 to 2 μm.

The above mentioned combinations of glass and plastics materials have been either rigid products, or the proportion of glass fibres or glass powder therein has been deliberately kept low because the plastics film has been required to assume certain new properties without substantial effect upon its original properties. Thin glass foils have the significant drawback of being very easily destroyed, whereas several plastics films have, among others, the disadvantage of being permeable to gas or vapour, or that their dimensional stability is absolutely insufficient for many purposes, particularly under the influence of heat.

The present invention provides a flexible composite material consisting of a glass foil coated on one or both surfaces with plastics material, the glass foil ranging in thickness from 4 to 200 μm and the or each layer of plastics material ranging in thickness from 2 to 200 μm. Such a composite material is distinguished by very good dimensional stability, even under heat influence, by impermeability to gases and vapours, and by a high degree of flexibility which mitigates the risk of destruction. Moreover, the material does not suffer irreversible changes under moderate heat influence.

A composite foil according to the invention therefore does not have the disadvantages of foils consisting only of glass or plastics material. Surprisingly, the novel material possesses a dimensional stability which does not differ, or only slightly, from that of glass alone, in spite of the plastics layer present (glass: between 0.4 and

1.0×10^{-5} °C^{-1}; in the case of plastics material, e.g., in the form of polyethylene terephthalates, the coefficient ranges from about 1.7×10^{-5} to 2.7×10^{-5} °C^{-1}). No irreversible changes of the material under the influence of normal fluctuations in temperature were observed. After being heated, the composite material reverts completely to its original dimensions.

As a further advantage over purely plastics films, a composite foil of the invention is absolutely impermeable to vapours and gases and is highly flexible. Thus, the fragility of thin glass plates, which is a very serious drawback, is eliminated by the composite material of the invention.

In a preferred embodiment, the glass foil of the composite material has a thickness in the range 20 to 100 μm, and the plastics film has a thickness in the range 10 to 100 μm, preferably 20 to 50 μm.

Although it is in principle possible to use plastics films of different thicknesses when both surfaces of the glass foil are to be covered, it has proved to be of advantage for the two plastics films to be of the same thickness and of the same material.

For the production of the composite material, in principle all plastics materials can be used which are capable of being combined with the glass foil, by extrusion coating, or in the form of films applied by means of a suitable adhesive, e.g. a polyurethane adhesive, or by means of an adhesion-improving agent, e.g., isocyanates, or by the application of a coating in the form of a dispersion or solution, if desired with the aid of an adhesion-improving agent. The following materials are suitable, for example: polyolefins, polyvinyl chloride, polyamides, polyvinylidene chloride, regenerated cellulose, cellulose acetates, polystyrene or mixed polymers or copolymers of these compounds. In view of their particularly high mechanical strength, polyesters, particularly polyethylene terephthalates, are preferably employed. A combination of the glass foil with mono- or biaxially stretched films has proved to be particularly advantageous.

For some purposes, e.g. when the composite material is to be made heat-sealable or weldable for use in the production of shaped articles, such as packages, the use of commercially available composite films, e.g. polyester/polyethylene laminates, has been found advantageous for coating the glass foil. In many cases, it is not necessary for the layer of plastics film to have a particularly low coefficient of thermal expansion, but for the use of the composite material for example as drawing material, the coefficient of thermal expansion should be as low as possible. For these purposes, composite foils are produced whose coefficient of total thermal expansion in any direction in the plane of the material is advantageously below 10^{-5} °C^{-1}.

The invention further provides processes for the production of the composite material. In one of these processes a glass foil ranging in thickness as specified is provided on one or both surfaces with a layer of plastics material ranging in thickness as specified, by extrusion coating, or by coating from a dispersion or a solution, and the resulting composite material is then solidified.

Extrusion of the plastics material is performed by means of known devices, particularly slot dies, the material being preferably extruded as a continuous operation upon travelling webs of glass foil. Adhesion-improving layers may be applied to the glass foil before the plastics material is extruded thereon.

In a further process an adhesive layer ranging in thickness from 1 to 10 μm, preferably from 2 to 5 μm, is applied, either to one or to both surfaces of a glass foil ranging in thickness from 4 to 200 μm and/or to one surface of one or two prefabricated plastics films ranging in thickness from 2 to 200 μm, the foil and the film, or the foil and a film on each side, are then pressed together with coated surface or surfaces in contact and the resulting composite material is solidified.

Preferably prior to the application of an adhesive layer, and/or prior to pressing together, an adhesion-improving agent is applied to any uncoated surface.

When an adhesive or an adhesion-improving agent is used in the production of the composite material by laminating a plastics film to the glass foil, the adhesive and/or the adhesion-improving agent is applied by means of known devices, a continuous operation, in which the glass foil is combined with the plastics film drawn from a reel, being preferable to a cyclic operation. Coating with a dispersion or a solution is also performed by known means and mixed polymers or copolymers of plastics materials may be used, if desired.

In some cases, it has proved to be of advantage to subject the composite material to a heating treatment in order to thermostabilize the plastics material. The thin composite materials have the advantage of being easily permanently deformed under the influence of heat, so that specific shaped articles can be produced having among others the property of returning to their original shape after having been compressed and then released.

Owing to their dimensional stability, which is excellent even under heat influence, the composite foils according to the invention have been found to be particularly suit-

able as drawing films, from which copies can be prepared which are exceptionally accurate to size. Whereas in the case of the hitherto used drawing films, in particular when they had been stored under heat influence, irreversible changes in the dimensions, resulting in significant deviations in the copies, occurred quite frequently and caused considerable difficulties, e.g. in the case of constructional drawings for precision instruments or in the cartographic art, the novel composite foils do not have such defects. Printing plates, in which these composite foils are used as base materials, are also distinguished by a very good dimensional stability.

A further preferred field of application is the use of the gas- and vapour-impermeable foil for packaging purposes. Thus, the composite material of the invention may be processed into sealable flat-folding bags or other shaped articles, which may even be made round, because of the favourable bending radius of the novel material. It has been found that the foil is particularly suitable for packaging goods which tend to become dry or to lose their aroma. By the material of the invention, the production of small, handy packages, which are as completely impermeable as known aluminium/plastics film laminates, has been made possible for the first time. The material of the invention retains its transparency however, a quality which is highly desirable for many commercial purposes and by which mistakes as to the contents of a package can be avoided.

As another application, a material of the invention can be used as a transparent, flexible protective cover for objects which have to be protected from the detrimental effects of humidity and/or gases. As an example, valuable paintings may be wrapped in such covers.

The following Examples illustrate the invention:

Example 1

A travelling web of glass foil (coefficient of thermal expansion at 100°C: $0.107 \times 10^{-4}\,{}^{\circ}C^{-1}$) of a thickness of 100 μm is coated on both surfaces with a polyethylene terephthalate film of 50 μm by extrusion of a melt of the latter material from a slot die. The composite foil thus produced could be bent several times to a bending radius of about 1.5 cm without destroying the glass foil. An attempt to bend an original glass foil of 100 μm thickness to the same bending radius failed, because the foil collapsed and broke. The coefficient of total thermal expansion of the composite material at a temperature between 20 and 50°C was $0.113 \times 10^{-5}\,{}^{\circ}C^{-1}$. Irreversible changes, such as occur with purely plastics films when heated, for example, to 90°C, were not observed. The composite material was absolutely impermeable to all gases and vapours.

Example 2

Low-pressure polyethylene films of 20 μm thickness were extruded upon both surfaces of a travelling web of glass foil of 50 μm thickness of the type described in Example 1. The properties of the composite material thus produced corresponded to the values stated in Example 1.

Example 3

A glass foil of 20 μm thickness of the kind used in Example 1 was coated on both surfaces with a 2 μm thick layer of an adhesive (ISARPLAST L 517), a product of Isar-Chemie, Munich 9, Germany) by means of a suitable applicator. Then both surfaces of the glass foil were covered with a biaxially stretched polyethylene terephthalate film of thickness 40 μm and, at a temperature of 80°C, the layers were pressed together for 2 minutes with a pressure of 20 kg/cm². After a thermal after-treatment at 90°C, which lasted two hours, a coefficient of total thermal expansion at a temperature of 20 to 50°C of $0.110 \times 10^{-4}\,{}^{\circ}C^{-1}$ was found. The composite material was absolutely impermeable to gases and vapours. No irreversible changes, caused by the action of heat, took place.

Example 4

A stationary glass foil of 150 μm thickness (coefficient of thermal expansion: $0.88 \times 10^{-5}\,{}^{\circ}C^{-1}$) was provided on both surfaces with layers of plastics films of 30 μm by applying to each surface six coatings of a polyvinylidene chloride dispersion and drying at an air temperature of 130°C. The coefficient of total thermal expansion at a temperature between 20 and 50°C was $0.93 \times 10^{-5}\,{}^{\circ}C^{-1}$. The other properties of the composite material thus produced corresponded to those above described.

Example 5

A composite material was produced as described in Example 1, with the exception that the material was subjected for 3 hours to an after-heating treatment at 90°C. The coefficient of total thermal expansion was $0.112 \times 10^{-4}\,{}^{\circ}C^{-1}$.

Example 6

A stationary glass foil (coefficient of thermal expansion: $0.85 \times 10^{-5}\,{}^{\circ}C^{-1}$) of a thickness of 50 μm was laminated on both surfaces to an 80 μm thick film of plasticized polyvinyl chloride using the adhesive "TEROKAL" 2183 M (a product of Teroson-Werke GmbH., Heidelberg, Germany) by applying the adhesive to the film

and then pressing the sandwich for 2 minutes at 80°C and 20 kg/cm² and subjecting it to a thermal after-treatment of 2 hours at 90°C. "Terokal" is a trademark. The composite material thus produced was bent to form a tube and welded by means of high frequency welding.

WHAT WE CLAIM IS:

1. A flexible composite material consisting of a glass foil coated on one or both surfaces with plastics material, the glass foil ranging in thickness from 4 to 200 μm and the or each layer of plastics material ranging in thickness from 2 to 200 μm.

2. A material as claimed in claim 1, in which the glass foil has a thickness in the range 20 to 100 μm.

3. A material as claimed in claim 1 or 2, in which the or each plastics layer has a thickness in the range 10 to 100 μm.

4. A material as claimed in claim 1 or 2, in which the or each plastics layer has a thickness in the range 20 to 50 μm.

5. A material as claimed in any one of claims 1 to 4, in which, in the case of two plastics layers, they each have the same thickness.

6. A material as claimed in any one of claims 1 to 5, in which the or each plastics layer consists of a polyester.

7. A material as claimed in any one of claims 1 to 5, in which the or each plastics layer consists of polyethylene terephthalate film.

8. A material as claimed in any one of claims 1 to 7, having a coefficient of total thermal expansion in any direction in the plane of the material of less than 10^{-4} °C^{-1}.

9. A material as claimed in any one of claims 1 to 8, having, between glass foil and plastics film, an adhesive layer of a thickness of 1 to 10 μm.

10. A material as claimed in any one of claims 1 to 8, having, between glass foil and plastics film, an adhesive layer of a thickness of 2 to 5 μm.

11. A material as claimed in any one of claims 1 to 10, having an adhesion-improving agent disposed between glass foil and plastics film.

12. A material as claimed in claim 1, substantially as described herein.

13. A process for the production of a composite material as claimed in any one of claims 1 to 8, wherein a glass foil ranging in thickness as specified is provided on one or both surfaces with a layer of plastics material ranging in thickness as specified, by extrusion coating, or by coating from a dispersion or a solution, and the resulting composite material is then solidified.

14. A process as claimed in claim 13, wherein the coating is by a continuous method.

15. A process as claimed in claim 13 or 14, wherein prior to the application of the plastics layer an adhesion-improving agent is applied.

16. A process for the production of a composite material as claimed in any one of claims 1 to 10, wherein an adhesive layer ranging in thickness from 1 to 10 μm is applied, either to one or to both surfaces of a glass foil ranging in thickness from 4 to 200 μm and/or to one surface of one or two prefabricated plastics films ranging in thickness from 2 to 200 μm, the foil and the film, or the foil and a film on each side, are then pressed together with coated surface or surfaces in contact and the resulting composite material is solidified.

17. A process as claimed in claim 16, wherein prior to the application of an adhesive layer, and/or prior to pressing together, an adhesion-improving agent is applied to any uncoated surface.

18. A process as claimed in any one of claims 13 to 17, wherein the composite material is subjected to a heating treatment with the object of thermostabilizing the plastics material.

19. A process as claimed in any one of claims 13 to 18, wherein the composite material is permanently deformed under heat action.

20. A process as claimed in claim 13 or 16, substantially as described in any one of the Examples herein.

21. A composite material, when made by the process claimed in any one of claims 13 to 20.

22. A material as claimed in any one of claims 1 to 11 and 21, in a form suitable for use as a film for drawing purposes or as a base for a printing plate.

23. A material as claimed in any one of claims 1 to 11 and 21, in a form suitable for use as a gas- and vapour-impermeable film for packaging purposes.

24. A material as claimed in any one of claims 1 to 11 and 21, in a form suitable for use as a transparent cover for articles such as paintings.

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